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PHASE EQUILIBRIA IN NITROPARAFFIN - HYDROCARBON SYSTEMS

A THESIS

Presented to

the Faculty of the Graduate Division

by

Stephen Chi Ping Hwa

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SYMBOLS

Letters

A	constant in activity coefficient equations, which is equal to the logarithm of the activity coefficient for hydrocarbon at mole fraction hydrocarbon of zero.
B	constant in activity coefficient equations, which is equal to the logarithm of the activity coefficient for nitroethane at mole fraction nitroethane of zero.
C	constant.
$\overline{H}$	partial molal enthalpy.
H^{O}	molal enthalpy of pure component.
P	pressure.
P^{O}	vapor pressure of pure compound.
R	gas constant.
T	absolute temperature.
t	temperature.
V	molal volume.
W	weight fraction.
X	mole fraction in liquid phase.
Y	mole fraction in gas phase.
γ	activity coefficient.
π	total pressure.

First Subscripts

C	at critical solution temperature.
H	of hydrocarbon.
i	of ith component.

M of the Margules equations.

N of nitroethane.

S of the Scatchard-Hamer equations.

V of the van Laar equations.

Second Subscripts

C at critical solution temperature.

H of hydrocarbon-rich layer.

N of nitroethane-rich layer.

Superscripts

' the constants A and B at the intersection point of Equations 11 and 12, or the temperature obtained by substituting the above A and B value in Equations 7 and 8.

" the constants A and B obtained by substituting experimental critical solution temperature in Equations 7 and 8.

Logarithm

ln base e

log base 10

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SUMMARY

The application of solvent extraction to certain systems has been found to be more economical than other separation processes, provided that a suitable solvent is available. The search for solvents which have potential use as extraction agents is a continuing one. Since nitroparaffins have miscibility characteristics similar to furfural and other organic solvents used in petroleum extraction, the consideration that nitroparaffins might have potential use in petroleum extraction field initiated this study of phase equilibria in nitroparaffin-hydrocarbon systems.

A series of qualitative tests were carried out on the miscibility of binary hydrocarbon-nitroparaffin systems. The tests covered 13 hydrocarbons (n-pentane, n-hexane, 2-methylpentane, 1-hexene, cyclohexane, cyclohexene, n-heptane, n-octane, 2,2,4-trimethylpentane, 1-octene, n-decane, benzene and toluene) and four nitroparaffins (nitromethane, nitroethane, 1-nitropropane, 2-nitropropane)--a total of 52 systems. From the tests, certain generalities were observed: (a) the critical solution temperature increases as the number of carbon atoms in the hydrocarbon increases, but it decreases as the number of carbon atoms in the nitroparaffin increases; (b) for hydrocarbons containing the same number of carbon atoms, the critical solution temperature decreases in the order--normal paraffin, isomer of normal paraffin, cyclic hydrocarbon and unsaturated hydrocarbon. These generalities suggested the possibility that some of the lower nitroparaffins such

as nitromethane and nitroethane, can be used to separate hydrocarbons of different structure and/or molecular weight. Based upon the above analysis, nitroethane and hydrocarbons including normal paraffins, monolefins and isomeric paraffins were chosen to be studied in this work.

The prediction of phase equilibria in a multicomponent system is theoretically possible if the data, such as activity coefficient, of the binary pairs involved in that system are known. Therefore, only binary systems were studied in this work. The mutual solubilities of these systems at various temperature intervals up to the critical solution temperature was determined by using both the analytical method and synthetic (cloud point) method. The uncertainty of the solubility data was estimated to be ± 0.002 weight fraction for most of the analytical data and $\pm 0.1\ ^{\circ}C.$ for most of the synthetic data. The binary systems and temperature range for which mutual solubility have been determined are tabulated in Table 1.

Table 1. The Binary Systems and Temperature Range of Mutual Solubility Determination

Systems	Temperature Range, °C.
n-Hexane - Nitroethane	2.9 to 29.3 (C. S. T.)*
2-Methylpentane - Nitroethane	2.05 to 26.7 (C. S. T.)*
1-Hexene - Nitroethane	-43 to -28.5 (C. S. T.)*
n-Octane - Nitroethane	4.2 to 41.3 (C. S. T.)*
2,2,4-Trimethylpentane - Nitroethane	1.8 to 29.5 (C. S. T.)*

Table 1. (cont.)

Systems	Temperature Range, °C.
1-Octene - Nitroethane	-27.5 to -4.6 (C. S. T.)*
n-Decane - Nitroethane	2.33 to 52.6 (C. S. T.)*

*Critical Solution Temperature.

These quantitative studies confirmed the qualitative tests and indicated that nitroethane might be useful as an extraction solvent in the separation of the hydrocarbons studied.

Mutual solubility data were used to calculate activity coefficients based on the van Laar, Margules and Scatchard-Hamer equations. The difference between the activity coefficients calculated by the van Laar and the Margules equations was negligible. However, in the dilute region, the activity coefficients calculated by the Scatchard-Hamer equations differed considerably from those calculated from the other two equations. The ratios of the constants A by B were in all instances less than two indicating that the van Laar equations should be applicable to these systems.

The plots of the van Laar constants A and B of each system versus the reciprocal of the absolute temperature gave straight lines at temperatures below the region of the critical point. Both plots started to deviate from the straight lines at three or four Centigrade degrees below the critical solution temperature. Thermodynamic conditions at the critical solution temperature were applied to examine the magnitude

of the deviation of the van Laar constants from the linear relation at that temperature.

The linear relationship between the van Laar constants and the reciprocal of absolute temperature permit the extrapolation of the van Laar constants beyond the experimental temperature range. Therefore, for the seven systems studied in this work, linear extrapolation to obtain the van Laar constants below experimental temperature should provide a good estimation. Since deviation from linearity has been found near the region of the critical temperature, the linear extrapolation up to critical temperature will introduce a slight error in the estimated constants.

Linear extrapolation of the van Laar constants into the temperature region above the critical solution temperature is somewhat more uncertain. However, in the absence of experimental vapor-liquid equilibrium data such extrapolation permits the estimation of the vapor-liquid equilibrium data for these seven systems.

CHAPTER I

INTRODUCTION

The process of solvent extraction has been extensively used in the petroleum industry. Among the organic solvents commercially used for this purpose are furfural, β,β-dichloroethyl ether, nitrobenzene, and phenol. These polar solvents exhibit different miscibilities with hydrocarbons, depending on the chemical characteristics of the hydrocarbons (1)*. Nitro-derivatives of lower paraffins, known as highly polar substances, have also been considered as potential solvents in this field. The use of nitromethane in the extraction of hydrocarbons has been studied by Trinh (2) and Kimura, et al. (3), and several ternary systems involving nitromethane and hydrocarbons have been investigated by Hunt, et al. (4) (5) and Francis (6), but data on nitroethane or higher nitroparaffins are lacking in the literature.

In order to obtain some knowledge of the miscibility of hydrocarbons and nitroparaffins, a test for this purpose including thirteen hydrocarbons and four lower nitroparaffins (a total of fifty-two binaries) has been made by H. Godbee and this author. From the results, tabulated in Table 8 in Appendix I, certain generalities can be observed: (a) the upper critical solution temperature of a nitroparaffin hydrocarbon system will increase as the number of carbon atoms in the hydrocarbon increases, but it will decrease as the number

---

*Numbers in parentheses refer to references listed in the Bibliography.

of carbon atoms in the nitroparaffin increases; (b) for hydrocarbons containing the same number of carbon atoms, the critical solution temperature decreases following the order: normal paraffin, isomer of the normal paraffin, cyclic hydrocarbon and unsaturated hydrocarbon. Similar generalities can be found in the data of Francis (7), where the critical solution temperature has been determined for hydrocarbons in over a hundred solvents, including most of the type used in petroleum extraction as mentioned in the first of this chapter. It seems that the difference in critical solution temperature between isomers and normal paraffins is larger in nitroparaffin solutions than in other solvents. The difference in critical solution temperature may not necessarily mean a difference in selectivity, as stated by Francis (7); it suggests, however, the possibility that nitroparaffins may be used to separate an isomer or an unsaturated paraffin from a normal paraffin. It was this possibility that initiated the interest in this study.

Since the prediction of phase equilibria in multicomponent systems are theoretically possible using data, such as activity coefficients, of binary pairs involved in that system (8), only binary systems of n-hexane - nitroethane, 2-methylpentane - nitroethane, 1-hexene - nitroethane, n-octane - nitroethane, 2,2,4-trimethylpentane - nitroethane, 1-octene - nitroethane, and n-decane - nitroethane were studied in this work.

The mutual solubility data for the seven systems were determined at various temperature intervals up to the critical solution temperature. The van Laar, Margules, and Scatchard-Hamer equations were used in the calculation of the activity coefficients from the mutual

solubilities. The activity coefficients at temperatures beyond the experimental temperature range can be estimated by extrapolation if the linear relationship between the constants of the activity coefficient equations and the reciprocal of absolute temperature is valid. This relationship, which had been studied by Benedict, et al. (9), Mertes, et al. (10), and Bethea (11), was also studied for these seven systems.

The determination of mutual solubility data at temperatures lower than room temperature was done mostly by means of gas chromatographic analysis. Synthetic (cloud point) method was used at temperatures above room temperature and also at some lower temperatures in order to check the agreement of two methods. The commonly used refractive index analysis was not applied to these systems because nitroethane and the seven hydrocarbons did not have a sufficiently large difference in their refractive index values.

CHAPTER II

THEORETICAL BACKGROUND

Calculation of activity coefficient.--The most frequently used equations relating activity coefficient with mole fraction are those developed by van Laar (12), Margules (13), and Scatchard and Hamer (14). These equations, after rearrangement by Carlson and Colburn (15), each contain two constants which are equal to the logarithm of the activity coefficients at infinite dilution. As an example, the van Laar equations relating the activity coefficients of the hydrocarbon and nitroethane with mole fractions are

$$\log \gamma_H = A_V/(1 + \frac{A_V}{B_V}\frac{X_H}{X_N})^2 \qquad (1)$$

$$\log \gamma_N = B_V/(1 + \frac{B_V}{A_V}\frac{X_N}{X_H})^2 \qquad (2)$$

where $A_V = \log \gamma_H$ at $X_H = 0$

$B_V = \log \gamma_N$ at $X_N = 0$

Scatchard and Hamer (14) have shown that for a partially miscible solution, constants A and B can be calculated from the knowledge of mutual solubilities. The equations derived by Carlson and Colburn (15) to calculate the van Laar constants from mutual solubilities are

$$\frac{A_V}{B_V} = \frac{\left(\frac{X_{HN}}{X_{NN}} + \frac{X_{HH}}{X_{NH}}\right)\frac{\log(X_{HH}/X_{HN})}{\log(X_{NN}/X_{NH})} - 2}{\left(\frac{X_{HN}}{X_{NN}} + \frac{X_{HH}}{X_{NH}}\right) - \frac{2X_{HN}X_{HH}}{X_{NN}X_{NH}}\frac{\log(X_{HH}/X_{HN})}{\log(X_{NN}/X_{NH})}} \tag{3}$$

$$A_V = \frac{\log(X_{HH}/X_{HN})}{\left(\frac{1}{1 + \frac{A_V}{B_V}\frac{X_{HN}}{X_{NN}}}\right)^2 - \left(\frac{1}{1 + \frac{A_V}{B_V}\frac{X_{HH}}{X_{NH}}}\right)^2} \tag{4}$$

Effect of temperature on activity coefficient.--Hougen and Watson (16) have derived an expression for the effect of temperature on activity coefficient as follows:

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_P = -\frac{\bar{H}_i - H_i^o}{RT^2} \tag{5}$$

where $\bar{H}_i - H_i^o$ is the partial molal enthalpy relative to the pure components at the temperature of the solution or the differential heat of solution. If data on heats of solution are available over the temperature range involved, the effect of temperature on activity coefficients can readily be shown by Equation 5. For many organic solutions the differential heat of solution at a constant composition are found to be only slightly affected by varying temperature (17), and Equation 5 can be integrated as follows:

$$\ln \gamma_i = (\bar{H}_i - H_i^o)/RT + C_1 \tag{6}$$

where C_1 is a function of pressure and composition. Benedict, et al. (9) have used a relation similar to Equation 6 to represent their data. Bethea (11) found that the activity coefficients calculated from the

mutual solubility data obtained in his work could be expressed by Equation 6. He also extrapolated Equation 6 from the partially miscible region to the temperatures above critical solution temperature in order to estimate the activity coefficients in the homogeneous region.

At infinite dilution (i.e. $X_N = 0$ or $X_H = 0$)

$$\log \gamma = A \text{ or } B$$

From Equation 6, it can be shown that

$$A = C_2/T + C_1 \tag{7}$$

$$B = C_2'/T + C_1' \tag{8}$$

where C_1, C_2, C_1' and C_2' are functions of composition and pressure. Mertes and Colburn (10) found that Equations 7 and 8 agreed well with experimental data.

The validity of Equations 7 and 8 was studied for the seven systems investigated in this study. For temperatures below the critical solution temperature where mutual solubilities could be used to calculate A and B, a direct check of Equations 7 and 8 was possible. For temperatures close to or at the critical solution temperature, the method in the following section of this chapter was used. Above the critical solution temperature, experimental activity coefficient data at some particular temperature are necessary to show the validity of Equations 7 and 8. These data are not available for the nitroparaffin hydrocarbon systems studied in this work.

Activity coefficients at critical solution temperature.--At critical solution temperature, Prigogine (18) derived the necessary and sufficient condition that

$$\frac{da_i}{dX_i} = 0$$

$$\frac{d^2a_i}{dX_i^2} = 0$$

Applying the above conditions to Equations 1 and 2 (van Laar equation) gives the following results (19):

$$\frac{A_{VC}}{B_{VC}} = \frac{(1 - X_{HC})(1 + X_{HC})}{X_{HC}(2 - X_{HC})} \tag{9}$$

$$A_{VC} = \frac{5.862(1 - X_{HC})}{(2 - X_{HC})^2(1 + X_{HC})} \tag{10}$$

Equations 9 and 10 can be combined into one equation by eliminating the parameter X_{HC}.

$$\phi(A_{VC}, B_{VC}) = 0 \tag{11}$$

By eliminating T from Equations 7 and 8, the following relation is obtained:

$$A_V = \frac{C_2}{C_2'} B_V - \frac{C_2 C_1'}{C_2'} + C_1 \tag{12}$$

Equations 11 and 12 when plotted using A_V as abscissa and B_V as ordinate will intersect at a point (A'_{VC}, B'_{VC}) which will be equal to the

value A''_{VC} and B''_{VC} obtained by substituting the experimental critical solution temperature in Equations 7 and 8, provided that the linear relations hold at temperatures up to the critical solution temperature. Dauphin (20) found that the relation of the A_V and B_V at critical solution temperature, which he obtained by extrapolating A_V and B_V calculated from mutual solubilities, was in good agreement with Equation 11. However, this agreement is actually a consequence of using Equations 3 and 4 to calculate A_V and B_V. Therefore, if the linear relation holds up to critical solution temperature, the using of Equations 3 and 4 will lead to the consequence that A'_{VC} and B'_{VC} is identical to A''_{VC} and B''_{VC}, respectively.

The above analysis is based on the assumption that the activity coefficients of the system do agree with the van Laar equations. The same procedure can also be applied to the system represented by the Margules or Scatchard-Hamer equations.

CHAPTER III

EXPERIMENTAL APPARATUS AND MATERIALS

Apparatus.--The mutual solubilities were determined by two methods, the analytical method and the synthetic (cloud point) method (21). The analytical method requires that equilibrium be attained between the two phases of the binary system. The mutual solubilities are then determined by analyzing the samples taken from each of the two liquid phases. The synthetic method determines the temperature at which phase separation occurred and disappeared in a binary system of known composition. The apparatus for the two methods are described as follows:

1. Analytical Method.

The essential features of the constant temperature bath and the equilibrium cylinder are shown in Figure 1. The bath--manufactured by Wilkins-Anderson Company, Chicago, Illinois--consisted of a pyrex jar of ten gallon volume, a stirrer, a refrigerator and a heater both controlled by a mercury thermo-regulator. Aqueous propylene glycol solution containing 60 per cent by weight of glycol was used as bath fluid. The bath was insulated with plexiglas and cotton. This unit was able to maintain a fixed temperature within one tenth of a centigrade degree. A thermometer with 0.1°C. subinterval, claimed by supplier to meet the requirements of National Bureau of Standards Circular 8, was used to obtain the bath temperature.

The equilibrium cylinder--a modified graduated cylinder of about

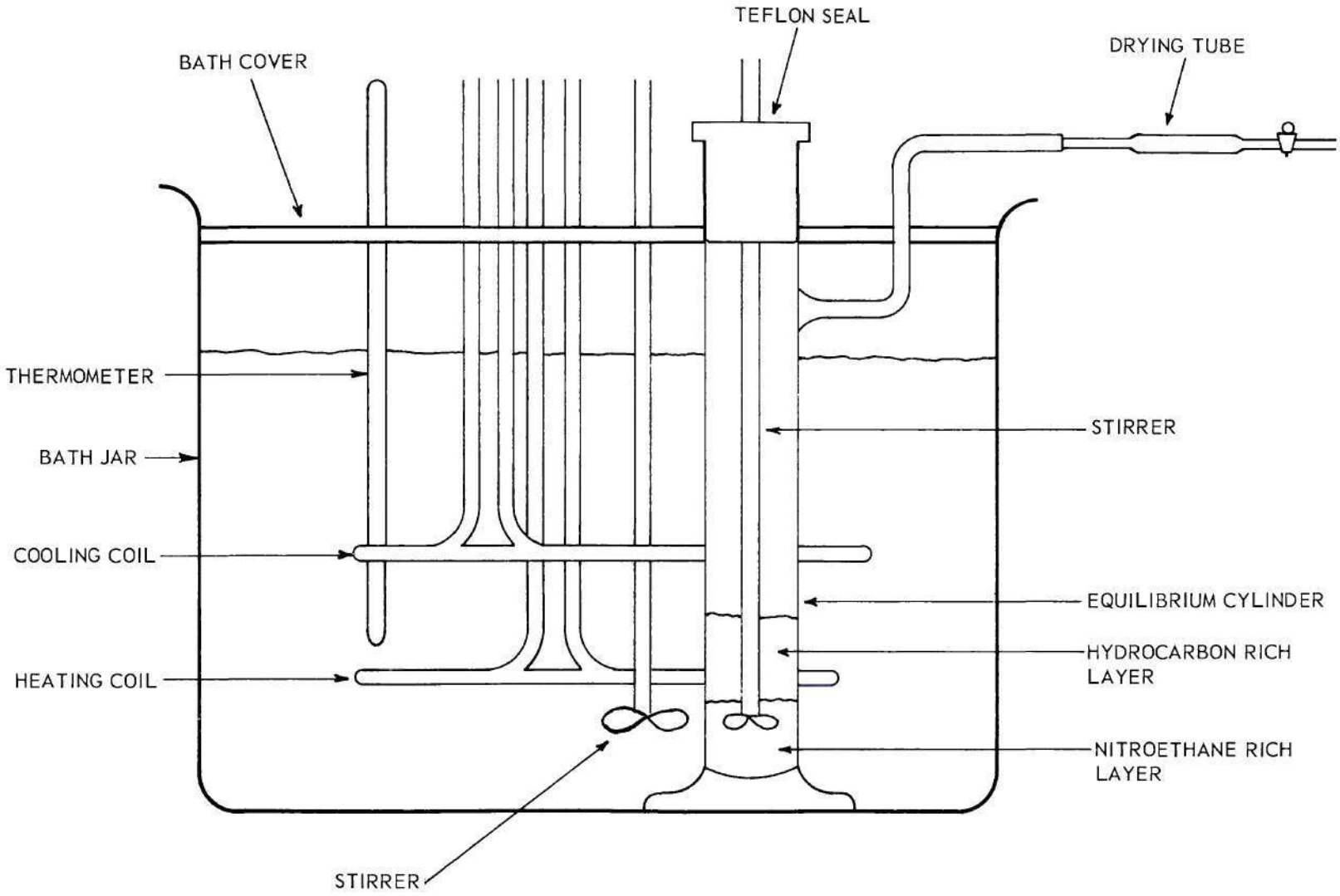

Figure 1. Constant Temperature Bath and Equilibrium Cylinder.

350 ml. volume--had a ground glass top, which was tightly fitted to a Teflon seal stirrer driven by a variable speed motor and also interchangeably fitted to a ground glass seat for the sampling pipette. When the top end was closed by the stirrer or the sampling pipette, the pressure inside the cylinder was balanced with atmospheric pressure through a drying tube which reduced the evaporation rate in the cylinder.

A Model 154-B Vapor Fractometer, manufactured by the Perkin-Elmer Corporation, Norwalk, Connecticut, was used for analysis; its operation was based on the principles of gas chromatography (22). Helium was used as carrier gas. Two two-meter partition columns*, filled with diisodecyl phthalate as stationary liquid, gave complete resolutions to all of the binary systems studied in this thesis except the n-octane - nitroethane and the 1-octene - nitroethane systems. A silver nitrate column** was found to give complete resolution to these two systems.

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*This column was designated as A-column by the supplier, Perkin-Elmer Corporation. The characteristics of this column for separating hydrocarbons were studied in a number of preliminary experiments. It was found that the group of hydrocarbons which could not be separated from each other by this column usually contained a monolefin, its saturated paraffin and a few isomeric paraffins. For example, normal heptane, 1-heptene, 2,2,4-trimethylpentane and cyclohexane constituted one of the groups. For hydrocarbons of different groups, the hydrocarbon of higher boiling point generally had longer retention time than the hydrocarbon of lower boiling point.

**This column, made by Olin M. Fuller, was a quarter inch copper tube with a length of six feet filled with 20.5 gram of a mixture containing 71.29 weight per cent of insulating brick powder, 26.33 weight per cent of triethylene glycol and 2.38 weight per cent of silver nitrate. The brick powder was prepared by grinding a Johns-Manville, C-22, insulating brick to a size between 40 to 60 mesh. The silver nitrate was dissolved in triethylene glycol before being mixed with brick powder. The characteristic of this column was mentioned in "Gas Chromatography," by Keulemans (23).

In order to obtain a sufficiently high peak from nitroethane, the column had to operate at least above 80°C. which was much above the proper column temperature for hydrocarbons that the retention time of hydrocarbon was too short to give a reproducible peak. Therefore, one of the phthalate columns mentioned above was used at 80°C. in series with the silver nitrate column (the phthalate column was connected after the silver nitrate column) for the analyses of n-octane - nitroethane and 1-octene - nitroethane systems. The detector of the Vapor Fractometer was a thermister thermal conductivity cell. The voltage change of this cell was plotted by a potentiometer recorder manufactured by Leeds & Northrup Company, Philadelphia. The sample was introduced into the Fractometer by the Micro-dipper, a capillary pipette, supplied by the manufacturer of Fractometer.

2. Synthetic (Cloud Point) Method

A 10.0 ml. volumetric cylinder suspended in the constant temperature bath was fitted with a cork with a thermometer inserted through the cork into the cylinder. The thermometer used here was the same as the one used in the constant temperature bath.

3. Refractive Index Determination

A Bausch & Lomb precision sugar refractometer (range 1.30 to 1.50) was used with a Precision "Temp-Trol" Water Bath which circulated constant temperature water through the Refractometer.

Materials.--All the hydrocarbons used in this study were donated by Phillips Petroleum Company, and the nitroparaffins were donated by Commercial Solvents Corporation. The materials were used as received

without further purification. In order to estimate the purity of the materials the refractive index of these materials were determined at 20°, 25° and 30°C. The refractive index values found and the corresponding values from literature are tabulated in Table 2. These materials were also analyzed by Vapor Fractometer at several temperatures. The diisodecyl phthalate column mentioned on page 11 was used for these analyses. The results of the analyses showed that n-octane, 2,2,4-trimethylpentane, 1-octene and n-decane gave no minor peak on the Fractogram*, but n-hexane, 2-methylpentane and nitroethane each had one minor peak, and 1-hexene had two minor peaks. The single minor peak which appeared with the nitroethane peak had the same retention time as 2-nitropropane, suggesting that 2-nitropropane might be the impurity in the nitroethane (24). The minor peaks of hydrocarbons were not identified. However, the areas of the minor peaks were in all instances less than 0.5 per cent of the area of the main peak which approximately represented the mole per cent of impurities in the material (22).

From the above analyses and the comparison of refractive index values with literature data, it was concluded that the materials used had a high purity.

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*The plot on the recorder chart showed the variation of voltage in the detector of the Fractometer.

Table 2. The Comparison of Refractive Index of the Starting Materials.

Material	Supplier	Grade	Refractive Index N_D (Data determined by this author) 20°C	25°C	30°C	Refractive Index N_D (Data from literature) 20°C	25°C	30°C
n-Hexane	Phillips Petroleum Co.	Pure*	1.37491	1.37240	1.36988	1.37486	1.37226 (25)	
2-Methyl-pentane	Ditto.	Technical**	1.37156	1.36897	1.36631	1.37145	1.36873 (25)	
1-Hexene	Ditto.	Technical**	1.38824	1.38540	1.38272	1.38788	1.38502 (25)	
n-Octane	Ditto.	Pure*	1.39746	1.39515	1.39288	1.39743	1.39505 (25)	
2,2,4-Tri-methyl-pentane	Ditto.	Pure*	1.39148	1.38918	1.38671	1.39145	1.38901 (25)	
1-Octene	Ditto.	Pure*	1.40872	1.40638	1.40389	1.40870	1.40620 (25)	
n-Decane	Ditto.	Pure*	1.41185	1.40977	1.40756	1.41189	1.40967 (25)	
Nitroethane	Commercial Solvents Co.	Redistilled	1.39195	1.38974	1.38739	1.39193	1.38973	1.38754 (26)

* 99 mole per cent minimum, claimed by the supplier.

** 95 mole per cent minimum, claimed by the supplier.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Analytical method.--This method was used to obtain mutual solubilities of a partially miscible solution by analyzing the samples taken from the two liquid layers.

The desired amount of hydrocarbon and nitroparaffin was poured into the equilibrium cylinder to prepare a solution of about 200 ml. total volume--approximately 100 ml. of volume of each phase in equilibrium. The time required to establish equilibrium in the solution at the bath temperature was determined by analyzing samples taken from the solution at different time intervals. It was found that the composition of both layers remained constant after eight minutes of stirring. Sixteen minutes of stirring was used in all experiments in this work.

After the solution was brought to equilibrium, the stirrer was abruptly stopped and removed. In place of the stirrer, the pipette seat and a sampling pipette for the lower layer was placed in position. In order to avoid contamination of the lower layer sample with solution from the upper layer, the above steps were executed so that the pipette was inserted into the solution when the solution was still swirling by the inertia from the stirring action. Also, a slight pressure was maintained in the pipette to keep the solution from entering the pipette until the two layers were clearly separated. The sample was then forced into the pipette by applying air pressure through the drying tube. The sample, with a volume of approximately eight

milliliters, was kept for analysis in a ten milliliter volumetric flask tightly closed by a ground glass stopper lubricated with stop-cock grease. The solution disturbed by the withdrawal of the pipette was then allowed to settle for fifteen minutes before the sampling of the upper layer. Since, at this time, the pipette only touched the upper layer, the measures to prevent contamination were not necessary.

In order to determine the composition of the collected samples, several calibration samples of known composition containing the same components as the unknown sample were analyzed by the Fractometer. The peak heights which appeared on the recorder (after correction for base line) were plotted against the composition of the known samples to obtain a calibration curve. Since the peak height was directly proportional to the concentration of the component (22), the calibration curve obtained was essentially a straight line which could be extrapolated to the origin as shown in Fig. 2. The peak height of the unknown sample gave a composition on the calibration curve; this composition was used as the composition of the unknown sample. It was decided to use the peak height of the minor component since the peak height of the minor component was more sensitive to the change of composition than the major component for the calibration curve. The accuracy of this method depended primarily upon a stable operating condition of the Fractometer during analysis. A small change in column temperature, flow rate or other operating conditions usually gave a significant change in peak height. Therefore, a known sample was introduced into the Fractometer from time to time to check the reproducibility of the operating conditions. The operating conditions of the Fractometer are tabulated in Table 16, Appendix II.

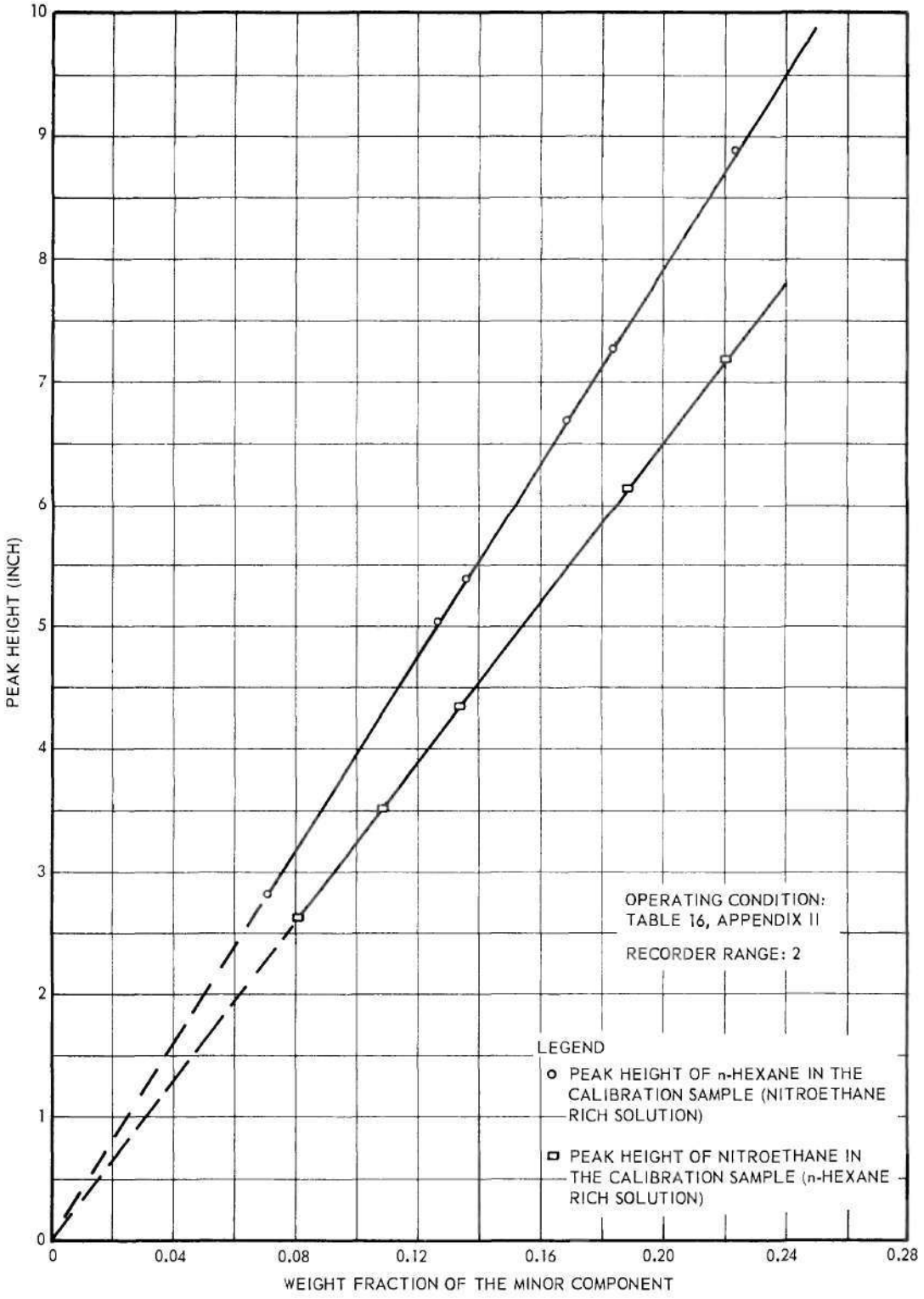

Figure 2. Calibration Curve. n-Hexane - Nitroethane System.

The mutual solubility at temperatures above room temperature could not be obtained by this analytical method because of phase separation which occurred in the sample after withdrawal from the solution. The following synthetic method was used for this temperature range.

Synthetic (Cloud Point) Method

Known weights of hydrocarbon and nitroparaffin were added to a 10 ml. graduated cylinder to make a solution of about six ml. of volume. The cylinder, closed by the cork and the thermometer, was then submerged into the bath. By repeated heating and cooling of the solution in the bath, the temperature at which the solution became turbid due to the forming of a second phase and the temperature at which the turbid solution became homogeneous were determined to such an accuracy that both temperatures agreed to within one tenth of a Centigrade degree. The average value of these two temperatures and the composition of the homogeneous solution gave a point on the curve of the mutual solubility vs. temperature plot.

CHAPTER V

EXPERIMENTAL DATA AND RESULTS

In order to check the analytical method against literature data and data from refractive index determinations, the nitromethane-cyclohexane system was studied. The results are tabulated in Table 3.

Table 3. Comparison of Mutual Solubility of Nitromethane-Cyclohexane System

Source of Data	W_{HH} 15	25	30 (°C)	W_{HN} 15	25	30 (°C)
Analytical Method				0.043	0.053	0.065
Weck & Hunt (5)		0.978			0.051	
Refractive Index	0.978	0.972	0.966	0.043	0.054	0.066

Vreeland and Dunlap (27) have determined the mutual solubility in the 2,2,4-trimethylpentane - nitroethane system from 25°C. up to critical solution temperature. The critical solution temperature (29.8°C.) reported by them agreed with the value of 29.5°C. obtained in this work. However, the mutual solubility data estimated from their plotted data (no tabulated data given) show serious discrepancies when compared with the values obtained in the present work, as is shown in Table 4.

Table 4. Comparison of Mutual Solubility of Nitroethane - 2,2,4-Trimethylpentane System

Source of Data	W_{HH} 25	27	28 (°C)	W_{HN} 25	27	28 (°C)
Vreeland & Dunlap	0.875	0.846	0.812	0.315	0.262	0.396
This Work	0.776	0.730	0.704	0.283	0.320	0.340

Discrepancies were also noted between their mutual solubility plot and ternary plot. At 25°C. and zero concentration of the third component (perfluorotri-n-butylamine), the ternary plot gave an estimated value of 0.78 for W_{HH} and 0.32 for W_{HN}. Therefore, it is possible that their mutual solubility data were misplotted.

An estimation of the uncertainty in the experimental data was based on: (1) the agreement between the data obtained by the analytical and synthetic methods, (2) the smoothness of the curve in the mutual solubility vs. temperature plot, (3) the reproducibility of the equilibrium composition of the phases, (4) the reproducibility of Vapor Fractometer analysis.

For most systems, the uncertainty was about ±0.002 weight fraction for the analytical data and ±0.1°C. for the synthetic data, except for the 1-hexene - nitroethane system which had low reproducibility in the equilibrium cylinder.

The mutual solubility data for the seven systems are tabulated in Table 9 through Table 15 in the Appendix. Plots of these data are shown in Figure 3 through Figure 9. The binary systems and temperature range for which mutual solubility has been determined are tabulated in

Table 1, page x. The mutual solubility datum determined by the synthetic method is reported in the tables as a single value of composition with an average value of two temperatures, because the appearance and disappearance of turbidity in the solution can not be attained at the same temperature, as mentioned previously. The mutual solubility data determined by the analytical method had a variation of ±0.05°C. in temperature as mentioned in page 9. However, the effect of this temperature variation on composition has been estimated and is expressed as the uncertainty in the composition. Therefore, the temperatures of the mutual solubility data are presented as single values. The composition in the analytical datum was an average value of three or more analyses in the Fractometer for each equilibrium sample; the duplication of analyses was for the purpose of checking the reproducibility of Fractometer. In some cases when more than one sample are drawn from the same layer at the same temperature in order to check the reproducibility of the equilibrium composition, the average value of the samples is presented. The variation of composition from different analyses mentioned above is expressed as the uncertainty of the composition in the tables.

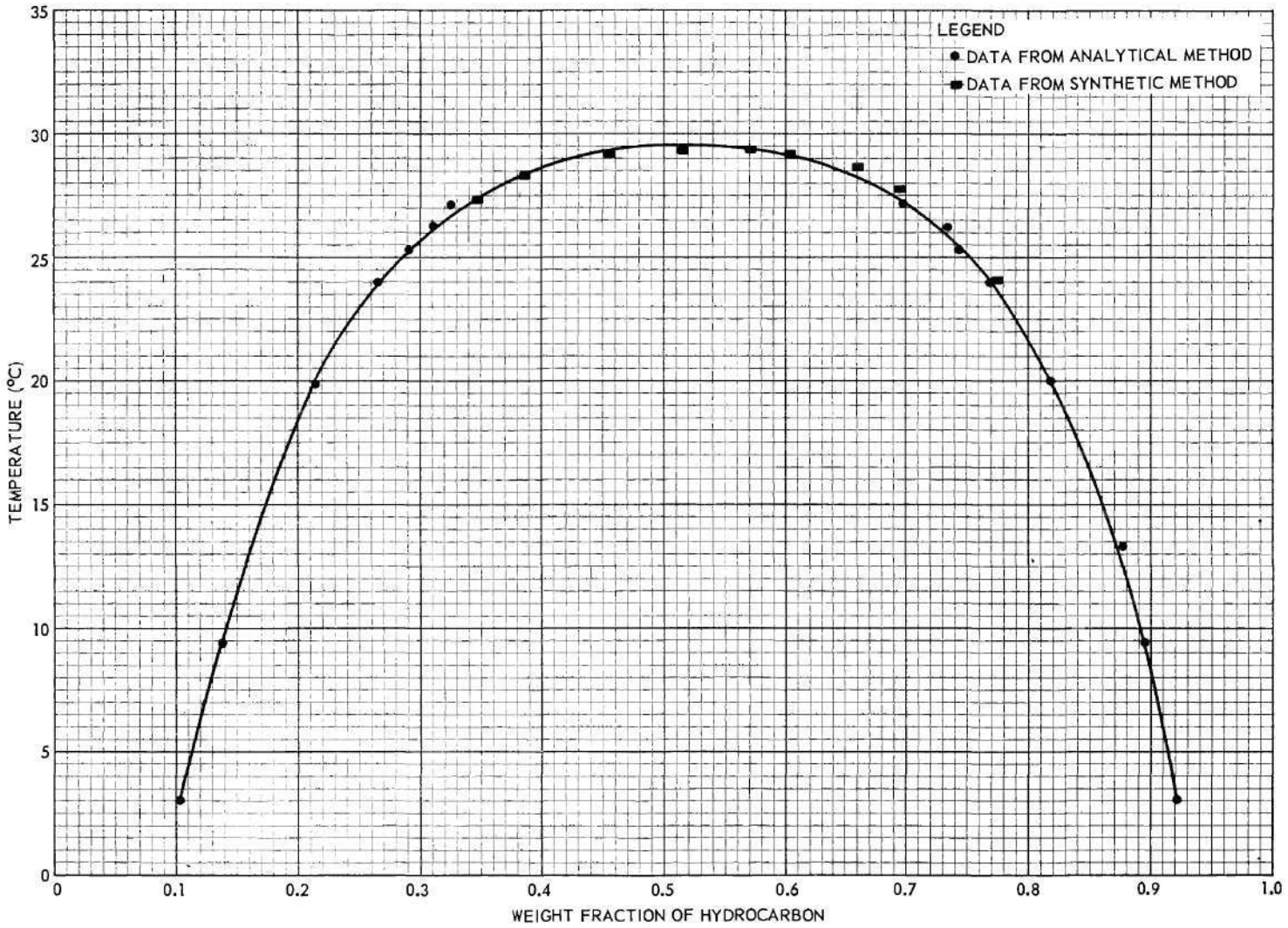

Figure 3. Mutual Solubility Versus Temperature.
n-Hexane - Nitroethane System.

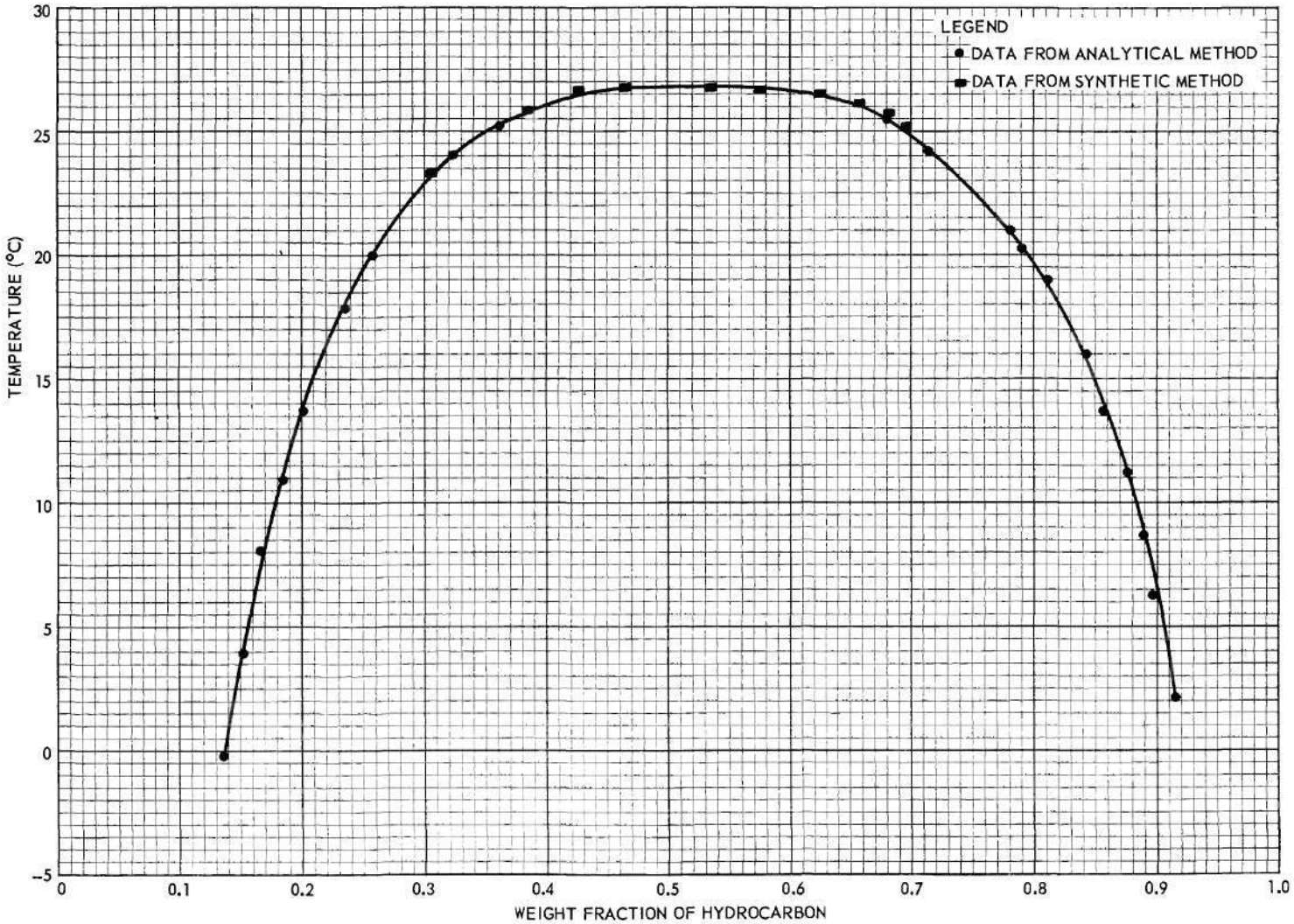

Figure 4. Mutual Solubility Versus Temperature.
2-Methylpentane - Nitroethane System.

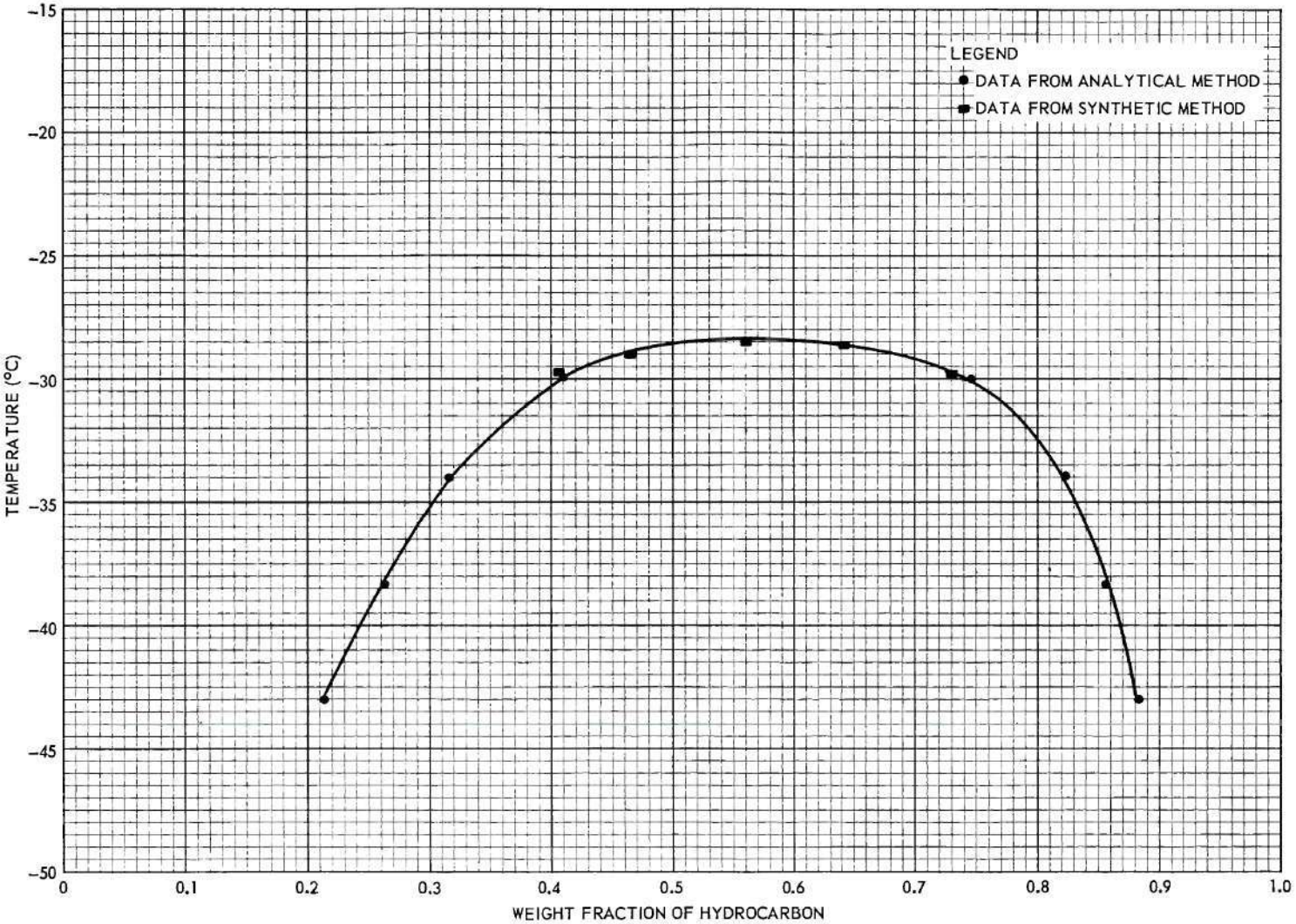

Figure 5. Mutual Solubility Versus Temperature.
1-Hexene - Nitroethane System.

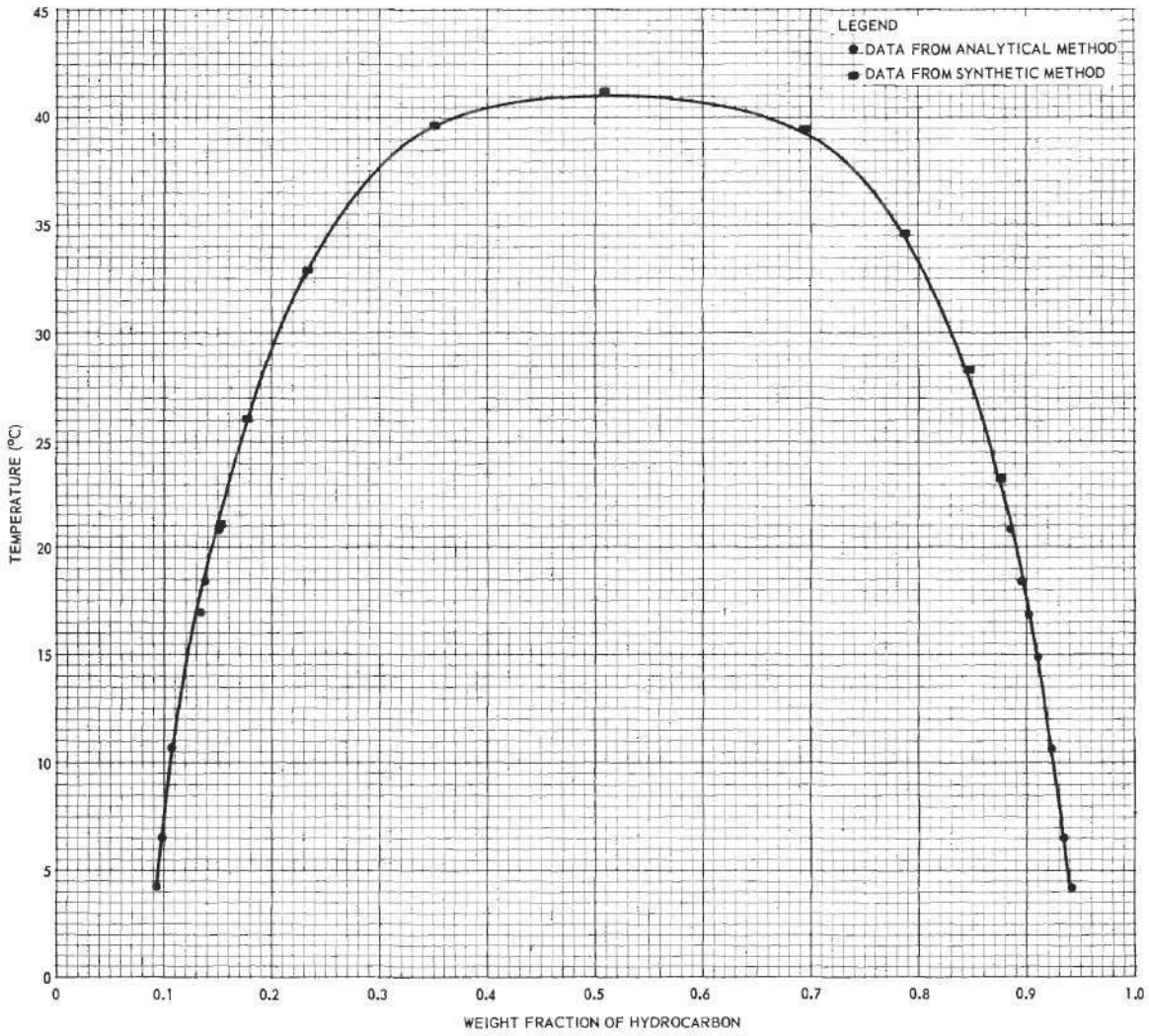

Figure 6. Mutual Solubility Versus Temperature.
n-Octane - Nitroethane System.

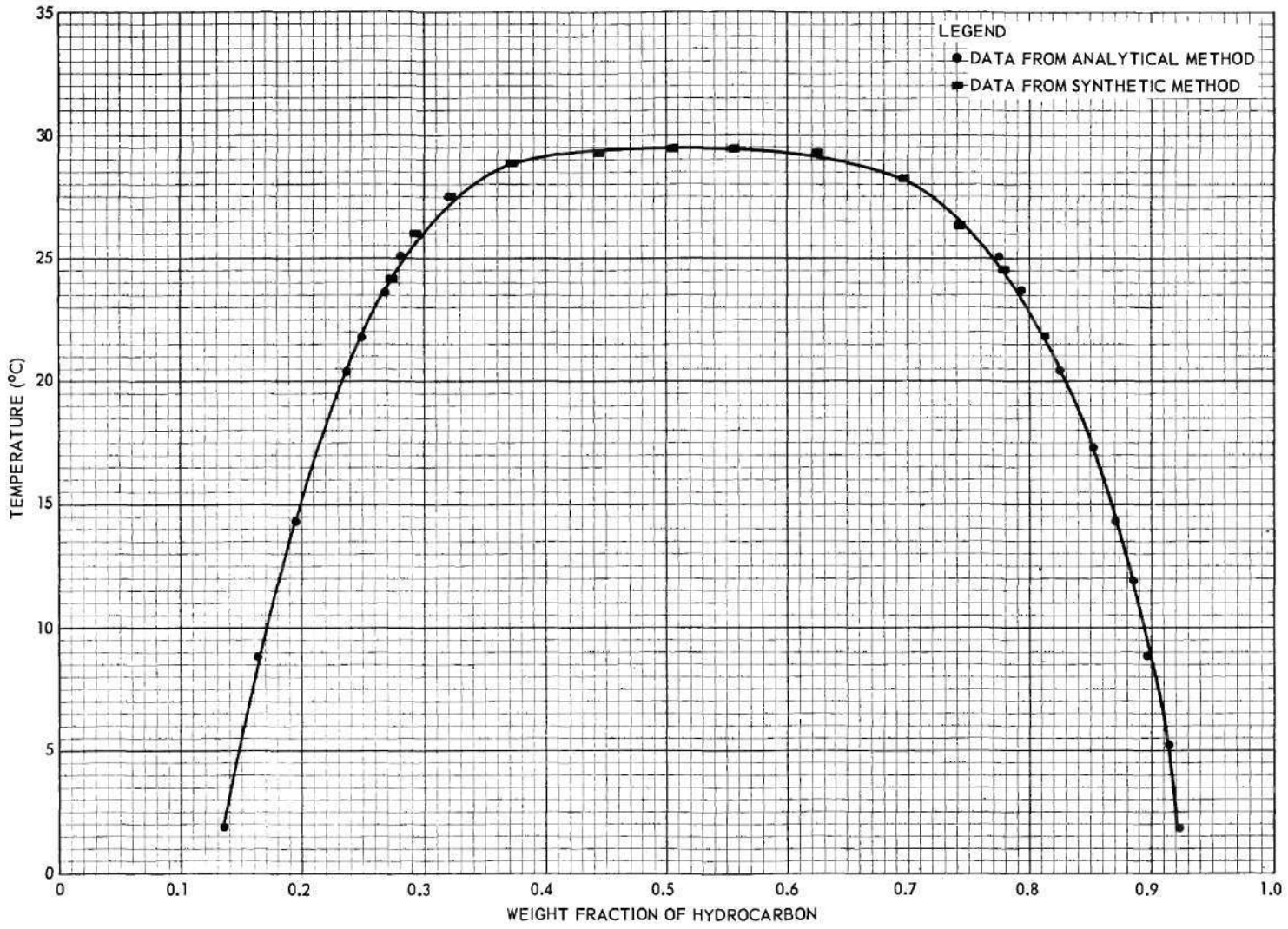

Figure 7. Mutual Solubility Versus Temperature.
2,2,4-Trimethylpentane - Nitroethane System.

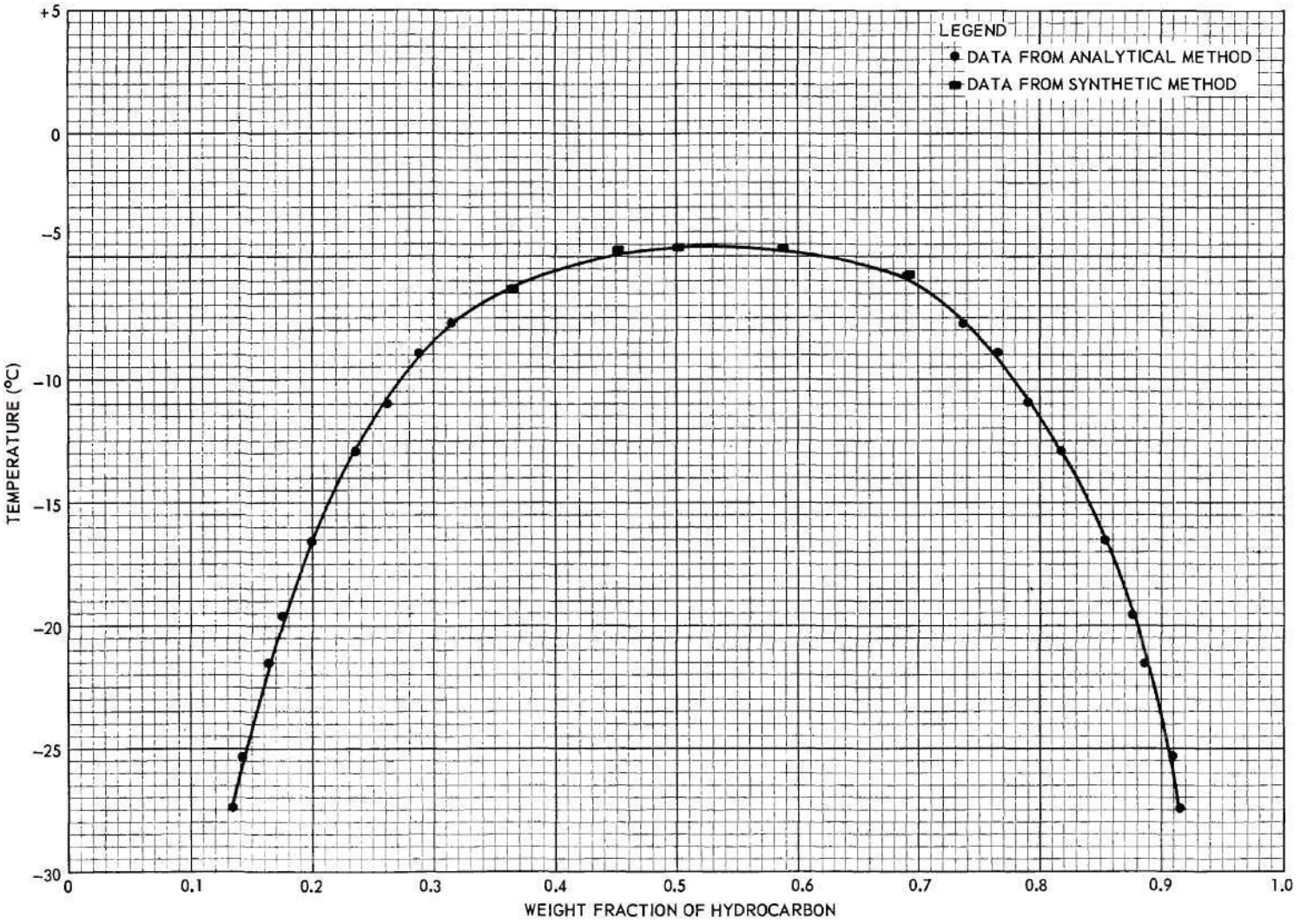

Figure 8. Mutual Solubility Versus Temperature.
1-Octene - Nitroethane System.

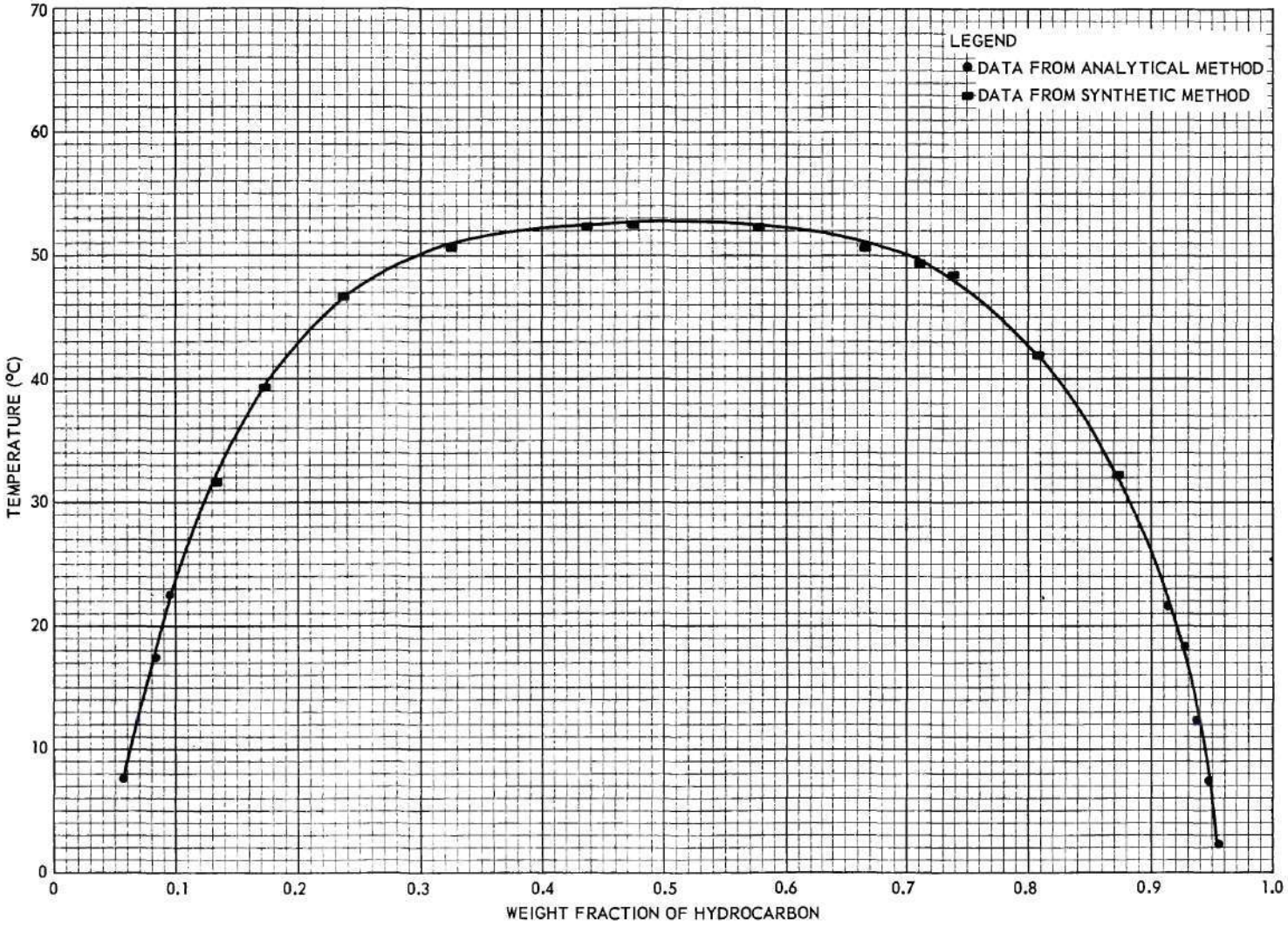

Figure 9. Mutual Solubility Versus Temperature.
n-Decane - Nitroethane System.

CHAPTER VI

ACTIVITY COEFFICIENT CORRELATION AND DISCUSSION

The validity of the van Laar, Margules and Scatchard-Hamer equations was investigated by Scatchard and Hamer (14), Carlson and Colburn (15) using experimental data to check the activity coefficient curve calculated from the three equations. Wohl (28) has summarized and extended their investigations into a description of the characteristics and limitations of these equations. He also showed that certain criteria could be used to select the appropriate equation for a binary system if some information about this system was known.

All three of the equations have been used by the author to correlate the data for n-hexane - nitroethane and 2-methylpentane - nitroethane systems.* The constants A and B at various temperatures are tabulated in Table 17 and Table 18 (Appendix III). The activity coefficients for the entire composition range have been computed from these constants and are tabulated in Table 24 and Table 25 (Appendix III). Both the van Laar and the Margules equations were used for the n-octane - nitroethane system. The calculated constants A and B at various temperatures are tabulated in Table 20 (Appendix III). For the systems 1-hexene - nitroethane, 2,2,4-trimethylpentane - nitroethane and n-decane - nitroethane only the van Laar equations were used. The calculated constants are tabulated in Tables 19, 21, 22, and 23 (Appendix

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*These and other computations have been carried out with the help of an IBM 650 computer.

III). The mutual solubility data used in these calculations were taken from the smoothed curve of the mutual solubility vs. temperature plot which had a scale larger than those shown in Fig. 3 to Fig. 9.

If the values of A_V and B_V are identical, the van Laar and the Margules equations reduce to the same expression (28). In these seven systems investigated, the ratios of the van Laar constants were close to unity, therefore the calculations made using the van Laar and the Margules equations gave almost identical results as shown in Tables 17, 18 and 20 (Appendix III). The constants A_S and B_S of the Scatchard-Hamer equations were slightly unsymmetrical but the ratios of the constants were still less than two as shown in Table 17 and 18 (Appendix III). The activity coefficients calculated by the Scatchard-Hamer equations differed in the dilute region from those calculated by the other two equations, as shown in Tables 24 and 25 (Appendix III). From these calculated data, it could be concluded that these seven systems were fairly symmetrical since the ratios of the van Laar constants were all less than 1.5. According to Wohl's analysis (28), such systems normally can be well described by the van Laar equations. Therefore, the following discussions were based on the data calculated from the van Laar equations. Although the discussions covered all seven systems, only the complete plot of n-octane - nitroethane systems was included in this thesis as an example.

From the plot of the van Laar constants, A_V and B_V, against the inverse of absolute temperature ^{o}K, as shown in Figure 10, the linear relations expressed by Equations 7 and 8 were found to apply to the seven systems at temperatures below the region of the critical point.

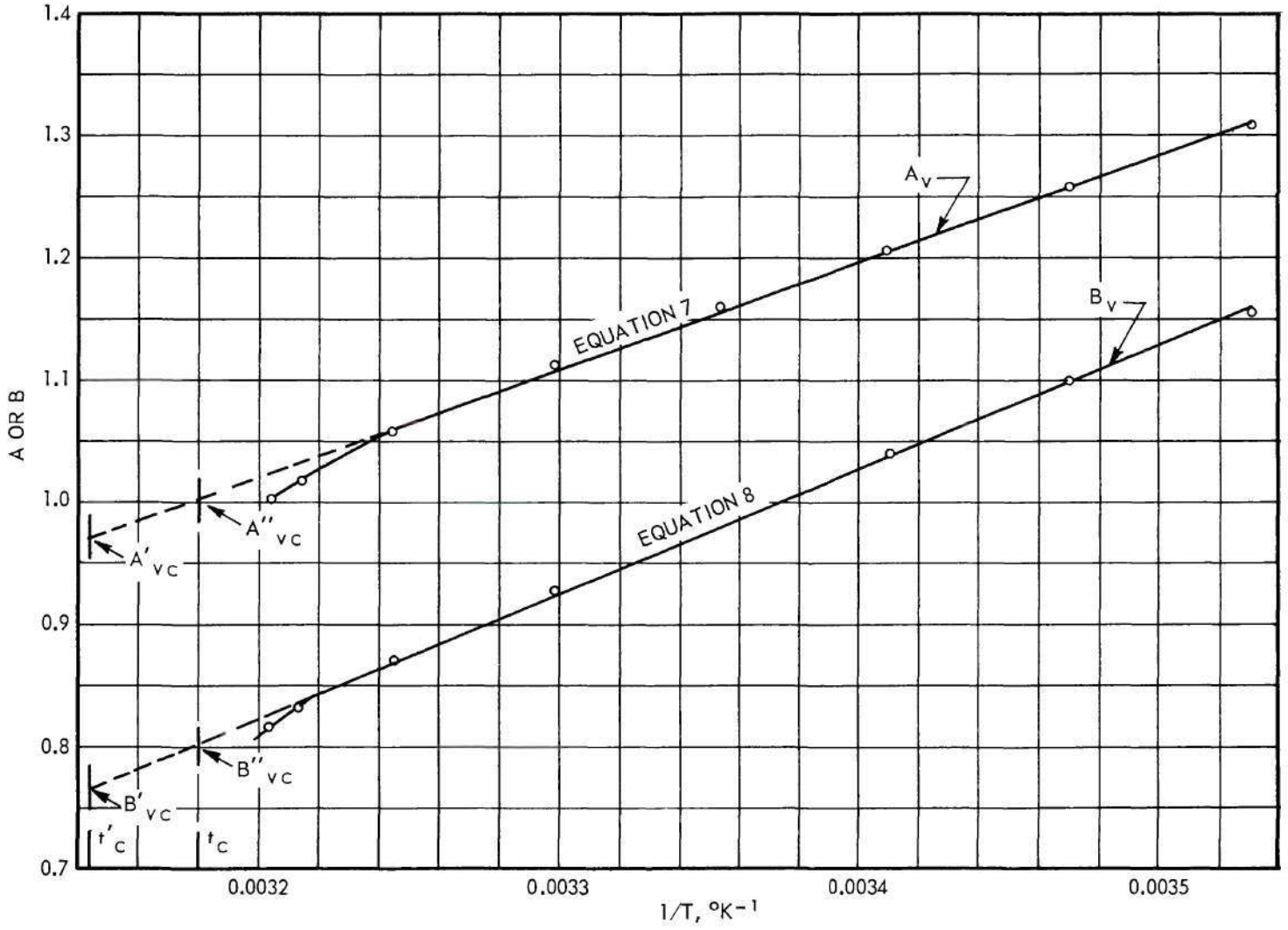

Figure 10. The van Laar Constants Versus Reciprocal Temperature. n-Octane - Nitroethane System.

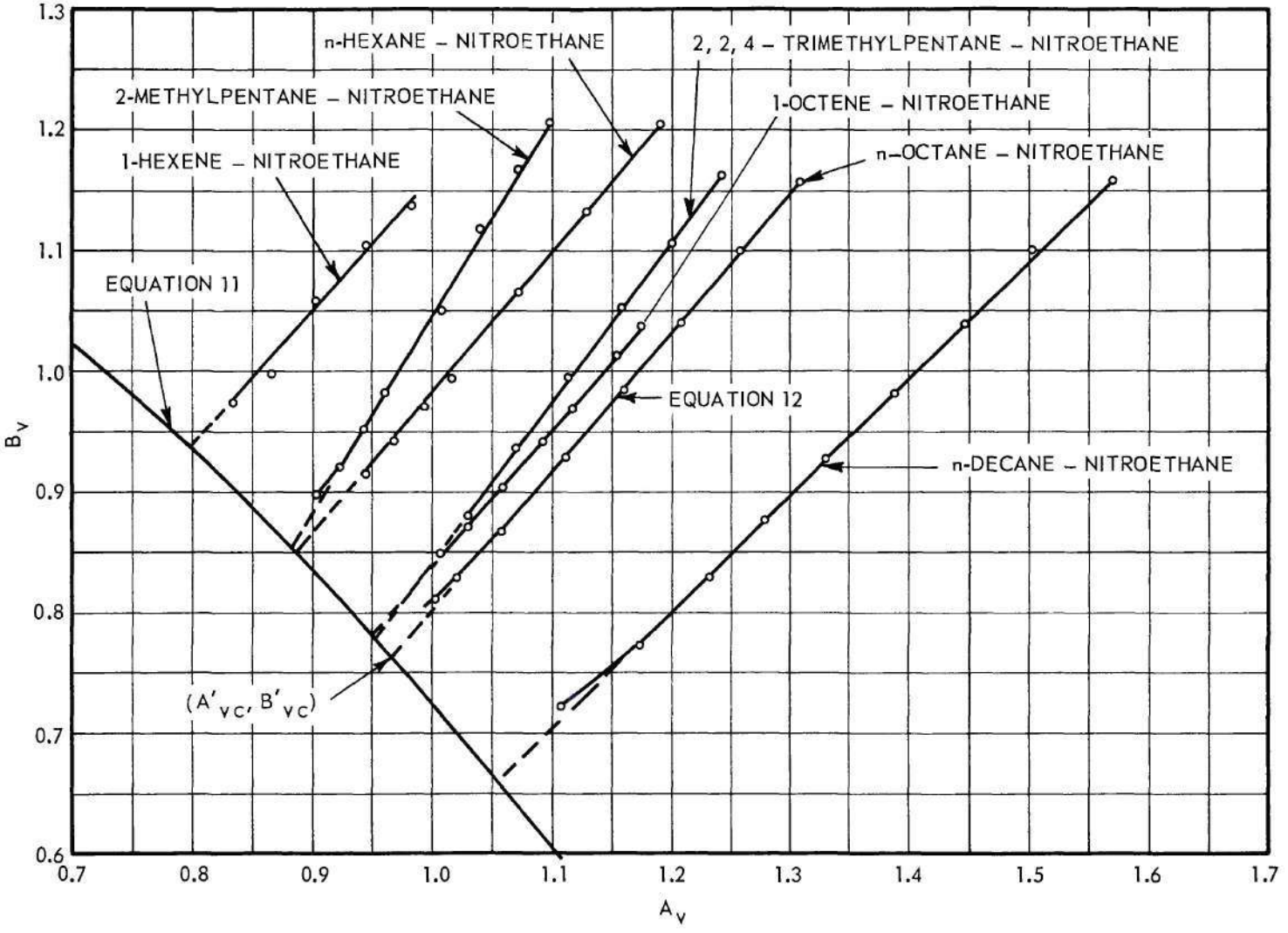

Figure 11. The van Laar Constants A_V Versus B_V.

The constants A_V and B_V began to deviate from the straight line about three or four degrees below the critical solution temperature. The approximate temperature at which deviation started is shown in Table 5.

Table 5. Comparison of Critical Solution Temperature and Deviation Starting Temperature

	Critical Solution Temperature °C.	Deviation Starting Temperature °C.
n-Hexane - Nitroethane	29.3	26
2-Methylpentane - Nitroethane	26.7	22
1-Hexene - Nitroethane	-28.5	-30
n-Octane - Nitroethane	41.3	37
2,2,4-Trimethylpentane - Nitroethane	29.5	25
1-Octene - Nitroethane	- 4.6	- 6
n-Decane - Nitroethane	52.6	46

The values of A_V and B_V became unreliable when the temperature approached the region close to critical solution temperature where the mutual solubility vs. temperature curves were so flat that no definite solubility could be read from the curves. At the critical solution temperature, Equations 3 and 4 become indeterminate since X_{HN} equals to X_{HH} and X_{NH} equals to X_{NN}. Therefore, the deviation at the critical solution temperature had to be estimated by the method discussed in the last section of Chapter II.

The straight line expressed by Equation 12 on Figure 11 was extrapolated to intersect with the curve plot of Equation 11 at a point

(A'_{VC}, B'_{VC}). On the extrapolation of Equations 7 and 8 on Figure 10, the values of A'_{VC} and B'_{VC} gave a temperature t'_C, and the experimental critical solution temperature t_C gave the values A''_{VC} and B''_{VC}. If the linear relationship had been held up to critical solution temperature, the t_C, A''_{VC} and B''_{VC} would have been equal to t'_C, A'_{VC} and B'_{VC} respectively. The values of t_C, t'_C, A''_{VC}, A'_{VC}, B''_{VC} and B'_{VC} obtained from the seven systems are tabulated in Table 6.

Table 6. Comparison of the van Laar Constants and the Critical Solution Temperature from Linear Extrapolation

	t_C	t'_C	A''_{VC}	A'_{VC}	B''_{VC}	B'_{VC}
n-Hexane - Nitroethane	29.3	31.2	0.909	0.886	0.874	0.848
2-Methylpentane - Nitroethane	26.7	30.4	0.912	0.882	0.899	0.853
1-Hexene - Nitroethane	-28.5	-26.6	0.816	0.795	0.958	0.936
n-Octane - Nitroethane	41.3	44.9	1.002	0.966	0.802	0.762
2,2,4-Trimethylpentane - Nitroethane	29.5	35.1	0.982	0.954	0.834	0.766
1-Octene - Nitroethane	- 4.6	- 2.5	0.971	0.948	0.810	0.782
n-Decane - Nitroethane	52.6	57.3	1.102	1.053	0.701	0.658

The discrepancy of these values indicated that the actual value of A_V and B_V at t_C, or A_{VC} and B_{VC}, did not equal to either A'_{VC} and B'_{VC} or A''_{VC} and B''_{VC}. The exact value of A_{VC} and B_{VC} could not be obtained; only the approximate magnitude could be estimated from the Figure 10 and Figure 11. From Figure 10, it was found that the plots of A_V and B_V calculated from the experimental data drifted downward from the

straight line when near the critical solution temperature. Therefore, A_{VC} and B_{VC} must be less than A''_{VC} and B''_{VC} respectively. From Figure 11, the plot of the curved part drifted upward which implied that A was less than A'_{VC} and B_{VC} was larger than B'_{VC}. The above analysis could be summarized as follows:

$$A_{VC} < A'_{VC} < A''_{VC}$$

$$B'_{VC} < B_{VC} < B''_{VC}$$

Using the value of the n-octane - nitroethane system in Table 6, the range of B_{VC} could thus be fixed:

$$0.762 < B_{VC} < 0.802$$

Knowing the range of B_{VC}, the range of A_{VC} was estimated from the plot of Equation 11 on Figure 11.

$$0.930 < A_{VC} < 0.966$$

Therefore, if the values of A''_{VC} and B''_{VC} obtained by linear extrapolation of Equations 7 and 8 were used in calculating the activity coefficients at t_C, an error would be introduced into the calculations. Since the maximum error in A''_{VC} was

$$A''_{VC} - 0.930 = 0.072$$

and in B''_{VC} was

$$B''_{VC} - B'_{VC} = 0.040$$

the maximum error in activity coefficients calculated from A''_{VC} and B''_{VC} was estimated in Table 7.

Table 7. Error in Activity Coefficient at t_C

X	0.00	0.05	0.1	0.2	0.4	0.6	0.8	0.9	1
Maximum Error %	8	6	5	5	3	2	0	0	0

The same analysis was applied to the other six systems. The maximum error in A''_{VC} and B''_{VC} of those systems was found to be in the same order of magnitude as the error in the n-octane - nitroethane system.

Experimental vapor-liquid equilibrium data are required for the further investigation of the choice of the van Laar equations and the validity of linear relationship. For example, the extrapolated constants A_V and B_V can be used to estimate the vapor-liquid equilibrium data from the following relations,

$$Y_H = \frac{P_H^\circ \gamma_H X_H}{\pi} \qquad Y_N = \frac{P_N^\circ \gamma_N X_N}{\pi}$$

The estimated value can be compared with the experimental vapor-liquid equilibrium composition data directly. However, the estimation of vapor-liquid equilibrium data by the above linear extrapolation method is also useful when no such data are available, as is the case of the seven systems studied in this work.

CHAPTER VII

CONCLUSIONS

From the results of this study of phase equilibria in nitroparaffin - hydrocarbon systems, the following conclusions may be drawn:

1. The critical solution temperature of nitroparaffin - hydrocarbon binary systems increases as the number of carbon atoms in the hydrocarbon increase, but decreases as the number of carbon atoms in the nitroparaffin increases. For hydrocarbons containing the same number of carbon atoms, the critical solution temperature decreases in the order--normal paraffin, isomeric paraffin, cyclic hydrocarbon and unsaturated hydrocarbons.

2. Experimental mutual solubility measurements were made for the seven binary systems: n-hexane - nitroethane, 2-methylpentane - nitroethane, 1-hexene - nitroethane, n-octane - nitroethane, 2,2,4-trimethylpentane - nitroethane, 1-octene - nitroethane and n-decane - nitroethane, at various temperatures up to critical solution temperature. The uncertainty in the solubility data was ± 0.002 weight fraction for most of the analytical data and $\pm 0.1^{\circ}C$. for most of the synthetic data.

3. The van Laar, Margules and Scatchard-Hamer equations were used to calculate the activity coefficients from the mutual solubility data. The activity coefficient curves calculated from these equations were fairly symmetrical since the ratios of the constants A and B were less than two. Therefore, the van Laar equations may be expected to represent the activity coefficients of these systems in the homogeneous region with good accuracy.

4. The linear relationship between constants A or B with the reciprocal of the absolute temperature was found to be valid from temperatures below the critical solution temperature to within a few degrees of this temperature. The linear relationship provides a means of estimating the van Laar constants or activity coefficients in the region where no experimental vapor-liquid or solubility data are available.

APPENDIX

APPENDIX I

QUALITATIVE MISCIBILITY TESTS FOR NITROPARAFFIN - HYDROCARBON SYSTEMS

Each system prepared for miscibility test consisted of a hydrocarbon and a nitroparaffin. Each pure component had an approximate volume of five milliliters. The solution was contained in a 10 ml. volumetric flask which was submerged in a constant temperature bath. The flask was kept in the bath for about 20 minutes with occasional shaking which was sufficient time to obtain equilibrium in the solution. If the solution appeared to be homogeneous, the concentration of this system was varied and reequilibrated at this temperature in order to assure that no phase separation occurred at any concentration at this temperature. The tests were executed at four different temperatures; -15°, 0°, 15° and 30°C. The occurrence of phase separation in these systems are tabulated in the following table.

Table 8. Miscibility Tests for Hydrocarbon - Nitroparaffin Systems.

	Nitromethane Temperature °C				Nitroethane Temperature °C				1-Nitropropane Temperature °C				2-Nitropropane Temperature °C			
	-15	0	15	30	-15	0	15	30	-15	0	15	30	-15	0	15	30
n-Pentane	P	P	P	P	P	P	M	M	M	M	M	M	M	M	M	M
n-Hexane	P*	P*	P*	P*	P*	P*	P*	M*	M*	M*	M	M*	M	M	M	M
2-Methyl pentane	P	P	P	P	P	P	P	M	M	M	M	M	M	M	M	M
1-Hexene	P	P	P	P	M	M	M	M	M	M	M	M	M	M	M	M
Cyclohexane	S*	S*	P*	P*	S*	P*	M*	M*	S*	M*	M*	M*	S	M	M	M
Cyclohexene	P*	P*	P*	P*	M*	M*	M*	M*	M*	M*	M*	M*	M	M	M	M
n-Heptane	P*	P*	P*	P*	P*	P*	P*	P*	P*	M*	M*	M*	M	M	M	M
n-Octane	P	P	P	P	P	P	P	P	P	M	M	M	M	M	M	M
2,2,4-Trimethylpentane	P*	P*	P*	P*	P*	P*	P*	M*	M*	M*	M*	M*	M	M	M	M
1-Octene	P*	P*	P*	P*	P*	M*	M*	M*	M*	M*	M*	M*	M	M	M	M
n-Decane	P	P	P	P	P	P	P	P	P	P	M	M	P	M	M	M
Benzene	S*	M*	M*	M*	S*	M*	M*	M*	S*	M*	M*	M*	S	M	M	M
Toluene	M*	M*	M*	M*	M*	M*	M*	M*	M*	M*	M*	M*	M	M	M	M

P: Partially miscible. M: Miscible. S: Solid form.

* Data determined by Herschel W. Godbee.

APPENDIX II

MUTUAL SOLUBILITY

Table 9. Mutual Solubility.

n-Hexane - Nitroethane System

Data from Analytical Method

Temperature, °C.	W_{HH}		W_{HN}	
2.90	0.921	±0.002	0.101	±0.002
9.40*	0.894	±0.002	0.136	±0.002
13.65	0.876	±0.002	---	---
19.95	0.818	±0.003	0.214	±0.004
24.00*	0.769	±0.003	0.265	±0.005
25.30	0.743	±0.003	0.290	±0.003
26.25	0.734	±0.003	0.310	±0.003
27.20	0.698	±0.003	0.324	±0.003

Data from Synthetic Method

Temperature, °C.	W_H	Temperature, °C.	W_H
26.1 ±0.2	0.3158	29.30 ±0.05	0.5703
27.4 ±0.1	0.3487	29.20 ±0.05	0.6017
28.3 ±0.1	0.3837	28.7 ±0.1	0.6610
29.20 ±0.05	0.4555	27.8 ±0.2	0.6950
29.30 ±0.05	0.5152	24.1 ±0.2	0.7737

Critical Solution Temperature 29.3°C.

*Duplicate samples had been drawn from each layer.

Table 10. Mutual Solubility.

2-Methylpentane - Nitroethane System

Data from Analytical Method

Temperature, °C.**	W_H	Temperature, °C., **	W_H
2.05	0.916 ±0.001	-0.35	0.137 ±0.001
6.30	0.899 ±0.001	3.80*	0.151 ±0.001
8.75*	0.890 ±0.002	8.00	0.169 ±0.001
11.20	0.877 ±0.002	10.85	0.186 ±0.002
13.75	0.857 ±0.002	13.70	0.201 ±0.002
15.95	0.843 ±0.002	17.80	0.236 ±0.002
19.00	0.812 ±0.002	20.00	0.259 ±0.002
20.25*	0.792 ±0.002	24.00	0.324 ±0.003
21.00	0.782 ±0.002	25.20	0.362 ±0.003
24.20	0.716 ±0.002	---	--- ---
25.50	0.680 ±0.002	---	--- ---

Data from Synthetic Method

Temperature, °C.	W_H	Temperature, °C.	W_H
23.4 ±0.1	0.3072	26.6 ±0.1	0.5783
25.8 ±0.1	0.3812	26.6 ±0.1	0.6239
26.7 ±0.1	0.4241	26.2 ±0.1	0.6594
26.7 ±0.1	0.4688	25.6 ±0.1	0.6819
26.7 ±0.1	0.5331	25.3 ±0.1	0.6969

Critical Solution Temperature 26.7°C.

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*Op. cit., page 42.

**Samples from two layers were taken at different temperatures.

Table 11. Mutual Solubility.

1-Hexene - Nitroethane System

Data from Analytical Method

Temperature, °C.	W_{HH}	W_{HN}
-43.0*	0.883 ±0.003	0.212 ±0.004
-38.4*	0.857 ±0.003	0.264 ±0.004
-34.0*	0.822 ±0.003	0.317 ±0.006
-30.0*	0.746 ±0.009	0.410 ±0.009

Data from Synthetic Method

Temperature, °C.	W_H	Temperature, °C.	W_H
-29.8 ±0.3	0.4081	-28.6 ±0.3	0.6411
-29.0 ±0.2	0.4650	-29.9 ±0.4	0.7295
-28.5 ±0.2	0.5602		

Critical Solution Temperature -28.5°C.

*Op. cit., page 42.

Table 12. Mutual Solubility.

n-Octane - Nitroethane System

Data from Analytical Method

Temperature, °C.	W_{HH}	W_{HN}
4.20	0.941 ±0.001	0.092 ±0.001
6.50*	0.935 ±0.001	0.097 ±0.001
10.70	0.924 ±0.002	0.107 ±0.001
14.85*	0.910 ±0.002	0.123 ±0.001
16.85	0.901 ±0.002	0.132 ±0.001
18.40*	0.895 ±0.001	0.137 ±0.001
20.80	0.885 ±0.001	0.150 ±0.001

Data from Synthetic Method

Temperature, °C.	W_H	Temperature, °C.	W_H
14.2 ±0.1	0.9143	41.3 ±0.1	0.5099
23.3 ±0.1	0.8770	39.6 ±0.1	0.3492
28.3 ±0.1	0.8451	32.8 ±0.1	0.2314
34.6 ±0.1	0.7863	26.0 ±0.1	0.1765
39.5 ±0.1	0.6912	21.0 ±0.1	0.1500

Critical Solution Temperature 41.3°C.

*Op. cit., page 42.

Table 13. Mutual Solubility.

2,2,4-Trimethylpentane - Nitroethane System

Data from Analytical Method

Temperature, °C.	W_{HH}	W_{HN}
1.80	0.923 ±0.001	0.134 ±0.001
5.12*	0.913 ±0.001	--- ---
8.80	0.898 ±0.001	0.161 ±0.001
11.90	0.885 ±0.001	--- ---
14.40*	0.870 ±0.001	0.193 ±0.001
17.42	0.851 ±0.001	--- ---
20.45	0.826 ±0.001	0.236 ±0.001
21.85*	0.814 ±0.001	0.248 ±0.002
23.63	0.793 ±0.001	0.268 ±0.002
25.01	0.774 ±0.001	0.279 ±0.003

Data from Synthetic Method

Temperature, °C.	W_H	Temperature, °C.	W_H
24.2 ±0.2	0.2721	29.5 ±0.1	0.5689
26.0 ±0.2	0.2910	29.4 ±0.1	0.6248
27.5 ±0.2	0.3201	28.3 ±0.1	0.6985
28.9 ±0.2	0.3711	26.4 ±0.2	0.7411
29.4 ±0.2	0.4412	24.6 ±0.2	0.7792
29.5 ±0.1	0.5051	---	---

Critical Solution Temperature 29.5°C.

*Op. cit., page 42.

Table 14. Mutual Solubility.

1-Octene - Nitroethane System

Data from Analytical Method

Temperature, °C.	W_{HH}	W_{HN}
-27.5	0.915 ±0.002	0.132 ±0.002
-25.4*	0.904 ±0.003	0.140 ±0.003
-21.6	0.885 ±0.003	0.162 ±0.002
-19.7*	0.875 ±0.004	0.174 ±0.002
-16.7*	0.851 ±0.002	0.199 ±0.002
-13.0	0.817 ±0.002	0.235 ±0.002
-11.0*	0.791 ±0.002	0.261 ±0.002
- 9.0	0.765 ±0.003	0.293 ±0.003
- 7.8*	0.738 ±0.004	0.312 ±0.004

Data from Synthetic Method

Temperature, °C.	W_H	Temperature, °C.	W_H
-6.45 ±0.05	0.3650	-4.60 ±0.05	0.5884
-4.70 ±0.05	0.4503	-5.80 ±0.05	0.6901
-4.65 ±0.05	0.5009	---	---

Critical Solution Temperature -4.60°C.

*Op. cit., page 42.

Table 15. Mutual Solubility.

n-Decane - Nitroethane System

Data from Analytical Method

Temperature, °C.**	W_{HH}	Temperature, °C.**	W_{HN}
2.33	0.956 ±0.001	7.80	0.057 ±0.001
7.40*	0.948 ±0.001	13.80	0.072 ±0.001
12.45	0.938 ±0.001	17.20	0.084 ±0.001
18.20*	0.924 ±0.001	22.40	0.096 ±0.001
21.50	0.912 ±0.001	---	---

Data from Synthetic Method

Temperature, °C.	W_H	Temperature, °C.	W_H
31.75 ±0.05	0.1320	52.30 ±0.05	0.5778
39.30 ±0.05	0.1738	50.80 ±0.05	0.6670
46.80 ±0.05	0.2387	49.32 ±0.05	0.7104
50.75 ±0.05	0.3246	48.60 ±0.05	0.7380
52.40 ±0.05	0.4380	42.00 ±0.05	0.8095
52.60 ±0.05	0.4753	32.35 ±0.05	0.8735

Critical Solution Temperature 52.6°C.

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*Op. cit., page 42.

**Op. cit., page 43.

Table 16. Operating Conditions of Vapor Fractometer

System	Column	Column Temp., °C.	Column Pressure psi	Helium Flow Rate cc./min.	Sample Size microliter
n-Hexane-Nitroethane	Two A-Column	150 ±0.2	20	35	2
2-Methylpentane-Nitroethane	Two A-Column	150 ±0.2	20	35	2
1-Hexene-Nitroethane	Two A-Column	150 ±0.2	20	35	2
n-Octane-Nitroethane	$AgNO_3$-Column and A-Column	87 ±0.1	10	45	5
2,2,4-Trimethylpentane-Nitroethane	Two A-Column	150 ±0.2	20	35	2
1-Octene-Nitroethane	$AgNO_3$-Column and A-Column	86 ±0.1	17	70	2
n-Decane-Nitroethane	Two A-Column	165 ±0.2	20	35	2

APPENDIX III. ACTIVITY COEFFICIENT.

Table 17. The van Laar, Margules and Scatchard-Hamer Constants. n-Hexane - Nitroethane System

Temperature, °C.	W_{HH}	W_{HN}	$V_H(25)$	$V_N(26)$	A_V	B_V	A_M	B_M	A_S	B_S
5	0.916	0.113	128.0	70.3	1.191	1.209	1.191	1.209	1.039	1.151
10	0.892	0.140	129.0	70.7	1.128	1.135	1.128	1.135	0.948	1.080
15	0.862	0.172			1.071	1.066	1.071	1.066		
20	0.819	0.215	130.0	71.5	1.016	0.997	1.016	0.997	0.808	0.929
20*	0.817	0.215			1.017	0.993	1.017	0.993		
20*	0.817	0.213			1.020	0.993	1.020	0.992		
22	0.797	0.238			0.993	0.970	0.993	0.970		
24	0.770	0.267			0.968	0.944	0.967	0.944		
26	0.733	0.303			0.944	0.914	0.944	0.914		
26*	0.738	0.303			0.942	0.920	0.942	0.920		
26*	0.733	0.306			0.941	0.915	0.941	0.915		
28	0.684	0.369	132.0	72.7	0.905	0.893	0.905	0.893	0.627	0.803

*Weight fraction arbitrarily chosen in order to show the variation of the constants with the change of weight fraction.

Table 18. The van Laar, Margules and Scatchard-Hamer Constants. 2-Methylpentane - Nitroethane System

Temperature, °C.	W_{HH}	W_{HN}	$V_H(25)$	$V_N(26)$	A_V	B_V	A_M	B_M	A_S	B_S
2	0.913	0.148	129.0	70.0	1.099	1.208	1.096	1.206	0.828	1.141
2*	0.915	0.148			1.097	1.216	1.095	1.214		
2*	0.913	0.146			1.103	1.208	1.101	1.206		
6	0.901	0.163			1.071	1.170	1.069	1.168		
10	0.883	0.180	130.0	70.7	1.046	1.121	1.045	1.120	0.768	1.047
15	0.848	0.212			1.008	1.050	1.008	1.049		
20	0.800	0.260	132.0	71.5	0.963	0.983	0.963	0.983	0.668	0.896
22	0.770	0.287			0.945	0.952	0.945	0.952		
24	0.728	0.323	133.0	71.8	0.926	0.917	0.926	0.917	0.633	0.826
24*	0.730	0.323			0.925	0.919	0.925	0.919		
24*	0.730	0.325			0.924	0.920	0.924	0.920		

*Op. cit., page 50.

Table 19. The van Laar Constants.

1-Hexene - Nitroethane System

Temperature, °C.	W_{HH}	W_{HN}	A_V	B_V
-43	0.883	0.212	0.983	1.138
-40	0.868	0.243	0.944	1.109
-36	0.838	0.290	0.901	1.062
-32	0.784	0.350	0.866	0.999
-30	0.746	0.410	0.833	0.976

Table 20. The van Laar and Margules Constants.

n-Octane - Nitroethane System

Temperature, °C.	W_{HH}	W_{HN}	A_V	B_V	A_M	B_M
10.0	0.926	0.105	1.310	1.152	1.307	1.148
10.0*	0.928	0.105	1.310	1.161	1.307	1.158
10.0*	0.926	0.107	1.304	1.153	1.301	1.149
15.0	0.911	0.124	1.257	1.097	1.253	1.092
15.0*	0.913	0.123	1.259	1.104	1.256	1.100
20.0	0.891	0.146	1.207	1.039	1.202	1.032
25.0	0.866	0.172	1.160	0.983	1.154	0.974
30.0	0.833	0.206	1.112	0.928	1.104	0.915
35.0	0.783	0.259	1.057	0.870	1.046	0.854
38.0	0.731	0.311	1.019	0.829	1.006	0.808
38.0*	0.734	0.311	1.018	0.832	1.005	0.813
38.0*	0.731	0.314	1.017	0.830	1.003	0.811
39.0	0.706	0.334	1.007	0.813	0.992	0.790
40.5	0.655	0.397	0.977	0.796	---	---

*Op. cit., page 50.

Table 21. The van Laar Constants.

2,2,4-Trimethylpentane - Nitroethane

Temperature, °C.	W_{HH}	W_{HN}	A_V	B_V
0	0.927	0.128	1.239	1.165
5	0.912	0.146	1.199	1.109
10	0.892	0.169	1.157	1.050
15	0.867	0.198	1.113	0.995
20	0.831	0.234	1.071	0.935
25	0.776	0.283	1.031	0.871
28	0.704	0.340	1.004	0.812

Table 22. The van Laar Constants.

1-Octene - Nitroethane System

Temperature, °C.	W_{HH}	W_{HN}	A_V	B_V
-28	0.915	0.130	1.233	1.121
-28*	0.913	0.130	1.233	1.113
-28*	0.915	0.132	1.227	1.121
-22	0.887	0.159	1.174	1.038
-20	0.875	0.172	1.151	1.011
-17	0.853	0.196	1.116	0.969
-15	0.837	0.214	1.092	0.944
-12	0.806	0.248	1.057	0.905
-12*	0.804	0.248	1.057	0.902
-12*	0.806	0.246	1.059	0.904
-10	0.780	0.275	1.034	0.878
- 8	0.748	0.312	1.007	0.854
- 6	0.698	0.371	0.974	0.828
- 6*	0.698	0.364	0.980	0.825

*Op. cit., page 50.

Table 23. The van Laar Constants.

n-Decane - Nitroethane System

Temperature, °C.	W_{HH}	W_{HN}	A_V	B_V
	—	—	—	—
10	0.945	0.063	1.569	1.158
15	0.934	0.076	1.502	1.101
20	0.920	0.089	1.447	1.041
25	0.903	0.106	1.387	0.985
30	0.882	0.126	1.331	0.930
35	0.857	0.148	1.282	0.879
40	0.826	0.177	1.230	0.830
45	0.775	0.220	1.173	0.771
50	0.705	0.295	1.105	0.725

Table 24. Activity Coefficients.

n-Hexane - Nitroethane System

	van Laar		Margules		Scatchard-Hamer	
At 5°C.	W_{HH} = 0.916	W_{HN} = 0.113				
X_H	γ_H	γ_N	γ_H	γ_N	γ_H	γ_N
0.0	15.5	1.00	15.5	1.00	10.9	1.00
0.1	9.36	1.03	9.26	1.03	9.23	1.01
0.2	5.82	1.11	5.82	1.11	6.35	1.08
0.4	2.69	1.55	2.69	1.55	2.80	1.54
0.6	1.55	2.69	1.55	2.69	1.53	2.82
0.8	1.12	5.82	1.12	5.82	1.10	6.05
0.9	1.03	9.31	1.03	9.31	1.02	9.19
1.0	1.00	15.8	1.00	15.7	1.00	14.2
At 10°C.	W_{HH} = 0.892	W_{HN} = 0.140				
0.0	13.4	1	13.4	1	8.87	1
0.1	8.21	1.03	8.21	1.03	7.82	1.01
0.2	5.29	1.11	5.29	1.11	5.61	1.07
0.4	2.56	1.51	2.56	1.51	2.64	1.49
0.6	1.52	2.55	1.52	2.55	1.50	2.62
0.8	1.11	5.30	1.11	5.30	1.10	5.38
0.9	1.03	8.28	1.03	8.28	1.02	7.99
1.0	1	13.6	1	13.6	1	12.0

Table 24. (cont.)

	van Laar		Margules		Scatchard-Hamer	
At 20°C.	W_{HH} = 0.819	W_{HN} = 0.215				
X_H	H	N	H	N	H	N
0.0	10.4	1.00	10.4	1.00	6.42	1.00
0.1	6.60	1.02	6.60	1.02	5.81	1.01
0.2	4.42	1.10	4.42	1.10	4.39	1.06
0.4	2.29	1.46	2.29	1.46	2.30	1.40
0.6	1.44	2.31	1.44	2.31	1.42	2.28
0.8	1.10	4.39	1.09	4.39	1.08	4.24
0.9	1.02	6.46	1.02	6.46	1.02	5.97
1.0	1.00	9.93	1.00	9.92	1.00	8.50
At 28°C.	W_{HH} = 0,684	W_{HN} = 0.369				
0.00	8.04	1.00	8.04	1.00	4.23	1.00
0.05	6.55	1.00	6.54	1.00	4.39	1.00
0.1	5.39	1.02	5.39	1.02	4.24	1.00
0.2	3.77	1.09	3.77	1.09	3.48	1.04
0.4	2.10	1.40	2.10	1.40	2.06	1.31
0.6	1.39	2.11	1.39	2.11	1.36	1.99
0.8	1.09	3.76	1.09	3.76	1.07	3.43
0.9	1.02	5.31	1.02	5.32	1.02	4.64
0.95	1.00	6.42	1.00	6.42	1.00	5.42
1.0	1.00	7.82	1.00	7.82	1.00	6.35

Table 25. Activity Coefficients.

2-Methylpentane - Nitroethane System

	van Laar		Margules		Scatchard-Hamer	
At 2°C.	W_{HH} = 0.913	W_{HN} = 0.148				
X_H	H	N	H	N	H	N
0.00	12.5	1.00	12.5	1.00	6.73	1.00
0.05	10.0	1.01	9.98	1.01	7.51	0.99
0.10	8.06	1.02	8.05	1.02	7.40	1.00
0.20	5.36	1.10	5.37	1.10	5.82	1.05
0.40	2.67	1.49	2.67	1.49	2.82	1.44
0.60	1.57	2.52	1.57	2.53	1.55	2.61
0.80	1.12	5.53	1.12	5.54	1.11	5.71
0.90	1.03	9.11	1.03	9.10	1.02	8.82
0.95	1.01	12.0	1.01	12.0	1.01	11.0
1.00	1.00	16.1	1.00	16.1	1.00	13.9
At 10°C.	W_{HH} = 0.883	W_{HN} = 0.180				
0.00	11.1	1.00	11.1	1.00	5.86	1.00
0.05	8.93	1.01	8.91	1.01	6.43	0.99
0.10	7.23	1.02	7.22	1.02	6.31	1.00
0.20	4.88	1.10	4.88	1.10	5.04	1.04
0.40	2.50	1.46	2.50	1.46	2.58	1.40
0.60	1.52	2.41	1.52	2.41	1.50	2.42
0.80	1.11	4.98	1.11	4.99	1.10	4.95
0.90	1.03	7.86	1.03	7.86	1.02	7.37
0.95	1.01	10.1	1.01	10.1	1.01	9.05
1.00	1.00	13.2	1.00	13.2	1.00	11.1

Table 25. (cont.)

	van Laar		Margules		Scatchard-Hamer	
At 20°C.	W_{HH} = 0.800	W_{HN} = 0.260				
X_H	H	N	H	N	H	N
0.00	9.19	1.00	9.18	1.00	4.66	1.00
0.05	7.43	1.01	7.43	1.01	5.01	0.99
0.10	6.07	1.02	6.07	1.02	4.91	1.00
0.20	4.18	1.09	4.18	1.09	4.02	1.04
0.40	2.25	1.42	2.25	1.42	2.25	1.34
0.60	1.44	2.23	1.44	2.23	2.14	1.41
0.80	1.10	4.21	1.10	4.20	1.08	3.95
0.90	1.02	6.21	1.02	6.21	1.02	5.54
0.95	1.01	7.68	1.01	7.68	1.01	6.60
1.00	1.00	9.62	1.00	9.61	1.00	7.87
At 24°C.	W_{HH} = 0.728	W_{HN} = 0.323				
0.00	8.44	1.00	8.44	1.00	4.29	1.00
0.05	6.84	1.01	6.84	1.01	4.55	0.99
0.10	5.61	1.02	5.61	1.02	4.42	1.00
0.20	3.89	1.09	3.89	1.09	3.64	1.04
0.40	2.14	1.41	2.14	1.41	2.11	1.32
0.60	1.40	2.15	1.40	2.15	1.37	2.03
0.80	1.09	3.88	1.09	3.88	1.07	3.56
0.90	1.02	5.55	1.02	5.55	1.04	4.15
0.95	1.01	6.74	1.01	6.74	1.02	4.86
1.00	1.00	8.26	1.00	8.26	1.00	6.70

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